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(54) 【発明の名称】 高強度ポリエチレン繊維

(57) 【要約】

【課題】 温度変化に対する繊維特性の変化が極めて少ない各種用途に好適な高強度ポリエチレン繊維を提供することを可能とした。

【解決手段】 繊維状態での極限粘度 $[\eta F]$ が5以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が 25 g/d 以上、弾性率が 800 g/d 以上であり、かつその繊維の動的粘弾性の温度分散測定における γ 分散の損失弾性率のピーク温度が -110°C 以下であり、さらに α 分散の損失弾性率のピーク温度が 100°C 以上である高強度ポリエチレン繊維。

【特許請求の範囲】

【請求項 1】 繊維状態での極限粘度 $[\eta F]$ が 5 以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が 25 g/d 以上、弾性率が 800 g/d 以上であり、かつその繊維の動的粘弾性の温度分散測定における γ 分散の損失弾性率のピーク温度が -110°C 以下であり、さらに α 分散の損失弾性率のピーク温度が 100°C 以上であることを特徴とする高強度ポリエチレン繊維。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、各種ロープ、釣り糸、土木・建築等のネット・シート材、化学フィルターやセパレータ用の布帛・不織布、防弾チョッキを始めとする防護衣料やスポーツ衣料、あるいはヘルメットや耐衝撃性コンポジット、スポーツ用コンポジット用の補強材料など、広く産業資材やテキスタイル用途に使用可能な高強度ポリエチレン繊維であり、温度変化の大きい環境下で使用される条件下でその性能の温度に対する変化、特に強度や弾性率などの力学特性において温度変化の少ない高強度ポリエチレン繊維に関する。

【0002】

【従来の技術】 超高分子量ポリエチレンを原料にして高強度・高弾性率繊維を得ようとする試みは、近年活発であり、非常に高い強度・弾性率を有する繊維が報告されている。例えば、特開昭 56-15408 号公報には、超高分子量ポリエチレンを溶剤に溶解し得られたゲル状の繊維を高倍率に延伸する、いわゆる「ゲル紡糸法」の技術が開示されている。

【0003】 「ゲル紡糸法」により得られた高強度ポリエチレン繊維は有機繊維としては非常に高い強度・弾性率を有し、さらには耐衝撃性が非常に優れる事が知られており、各種用途においてその応用が広がりつつある。このような高強度繊維を得る目的において、前出の特開昭 56-15408 号公報によれば、極めて高い強度と弾性率を有する素材を提供する事が可能であると開示されている。しかしながら一方で、高強度ポリエチレン繊維は温度による性能の変化が非常に大きいことで知られている。例えば、 -150°C 付近から温度を変化させてその引っ張り強度を測定すると、低温から温度上昇と共に徐々にその低下が観察され、特に室温以上、なかでも結晶分散と呼ばれる緩和機構が観察される 80°C 付近からその性能の低下が著しい。このような温度による性能の変化は本素材の温度変化の大きい環境下での使用を困難なものにしていた。

【0004】 従来、このような高強度ポリエチレン繊維の温度変化に因る力学特性の変化を制御するところみとして、特開平 7-166414 号公報に開示されているごとく、特定の分子量を持つ超高分子量ポリエチレン原料とその得られる繊維の分子量とを適正な範囲にするこ

とで、 -100°C 以下でのいわゆる極低温領域での振動吸収性を向上させる試みが示唆されているが、基本的に当該技術においては極低温での力学分散を大きくする。つまり、むしろ弾性率の変化を大きくする試みであり、本発明の目指す、力学特性の低下を少なくする試みとは相反するものであった。

【0005】 又、特開平 1-156508 号公報や特開平 1-162816 号公報には上記のゲル紡糸法において過酸化物質や紫外線照射などの手段により、高強度ポリエチレン繊維のクリープを低減する試みが開示されている。基本的に本手法によれば前述の γ 分散の力学分散が低くなる事が記され本発明の述べる好ましい方向ではあるが、両発明は高強度ポリエチレン繊維のクリープを改良するのが目的であり、力学特性の温度変化による変化を低減するものでは無かった。特に、通常 γ 分散における緩和強度が小さくなると、その緩和が起こる温度も高温にシフトするのが通例であり、従来の手法では本発明が目指すより温度の変化に対して力学特性の変化が少ないこと、すなわち γ 分散温度はより低温へかつ α 分散は高温であることが好ましいことから逆の方向であった。

【0006】

【発明が解決しようとする課題】 以上の観点に基づき、本発明は、常温で極めて優れた力学特性を有してかつ、温度変化による強度や弾性率などの力学特性において変化の少ない高強度ポリエチレン繊維を提供することを目的とする。

【0007】

【課題を解決するための手段】 即ち本発明は、繊維状態での極限粘度 $[\eta F]$ が 5 以上のエチレン成分を主体とするポリエチレン繊維であり、その強度が 25 g/d 以上、弾性率が 800 g/d 以上であり、かつその繊維の動的粘弾性の温度分散測定における γ 分散の損失弾性率のピーク温度が -110°C 以下であり、さらに α 分散の損失弾性率のピーク温度が 100°C 以上であることを特徴とする高強度ポリエチレン繊維である。

【0008】 本発明における超高分子量ポリエチレンとは、その繰返し単位が実質的にエチレンであることを特徴とし、少量の他のモノマー例えば α -オレフィン、アクリル酸及びその誘導体、メタクリル酸及びその誘導体、ビニルシラン及びその誘導体などとの共重合体であっても良いし、これら共重合物どうし、あるいはエチレン単独ポリマーとの共重合体、さらには他の α -オレフィン等のホモポリマーとのブレンド体であってもよい。特にプロピレン、ブテン-1 などの α -オレフィンと共重合体を用いることで短鎖分岐をある程度含有させることは本繊維を製造する上で紡糸・延伸において安定性を与えることとなり、より好ましい。しかしながらエチレン以外の含有量が増えすぎると延伸の阻害要因となる。従って、高強度・高弾性率繊維を得るという観点からはモ

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ノマー単位で5mol%以下であることが好ましい。もちろんエチレン単独のホモポリマーであっても良い。

【0009】本発明の骨子は、繊維状態で測定 of 動的粘弾性特性の温度分散における γ 分散の損失弾性率のピーク温度が -110°C 以下、好ましくは -115°C 以下であり、さらに α 分散の損失弾性率のピーク温度が 100°C 以上、好ましくは 105°C 以上であることを特徴とする。かかる特徴を有する高強度ポリエチレン繊維は常温での力学特性が極めて高くかつ、広い温度範囲においてその力学特性の変化が小さい。

【0010】本繊維の温度による性能の変化が少ないことは、2種の力学分散すなわち、 α および γ 分散の温度で確実に定義することができる。すなわち、力学分散の起こる温度域では通常、弾性率の著しい低下が観察される。高強度ポリエチレン繊維の場合、通常 -100°C 付近に γ 分散がまた、 85°C 付近に α 分散が観察される。この両者の温度を挟んで繊維を使用した場合、通常温度がこの両付近を通過するたびに極めて大きな弾性率および強度の変化をもたらす、各種製品設計上好ましくない。従って、通常は γ 分散温度以上および α 分散温度以下で、ある程度余裕を配慮して温度領域を設定し、その使用温度領域が決定される。したがって、 γ 分散温度はより低温へ、 α 分散温度はより高温であることは、上記の使用温度領域を広げる意味で非常に有意義である。

【0011】本繊維のように α 分散の温度が高いにも関わらず γ 分散のピーク温度が逆に非常に低温にあることは従来常識からは、極めて驚くべきことである。すなわち、 γ 分散にはもともと非晶と結晶との寄与があることが知られている。従来高強度ポリエチレン繊維においては、延伸倍率を高くしたり、結晶化を促進させたりすると、 α 分散を比較的容易に高温へ移行させることは可能である。このことは糸の微細構造がより結晶構造リッチになることを示唆している。この場合、 γ 分散を支配する構造も非晶から結晶に移ることになり、 γ 分散の温度も高温にシフトすることが通常であった。つまり、本発明で提供する繊維は微細構造的にも従来の常識とは反するものであると言える。さらに本繊維の α 分散のピーク温度は上記の延伸等の手段で得られる従来の高強度ポリエチレン繊維のそれが高々 95°C 程度であったのと比べて少なくとも 100°C 以上、好ましくは 105°C 以上と非常に高温である。また、 γ 分散においても上記のような高い α 分散温度を持つ繊維でなくても通常 90°C 以上を有する結晶性の高い繊維では、 -110°C より低温であることは困難であった。一部、例えば α 分散温度が 85°C 程度の繊維の場合、 γ 分散温度が -110°C 以下を示す場合があるが、これは繊維の構造がより非晶的になったためであり、本発明の目指す高結晶性(α 分散温度が高い)でありながら γ 分散温度もなおかつ低いという新規な繊維とは明確に区別することができる。

【0012】さて本発明に係る繊維を得る手法は当然な

がら新規でかつ慎重な手法を必要とするが、もちろん以下に示す例に限定されるものではない。すなわち本繊維を得る手法としては、前述の「ゲル紡糸法」が実際的手法として有効であるが、超高分子量ポリエチレンを成形して従来知られている高強度ポリエチレン繊維を得る手法であれば特に基本となる製糸技術は問わない。本発明においてまず重要な原料となるポリマーである。

【0013】すなわち、本発明においては、2種の超高分子量ポリエチレンを用いることが推奨される。この際、主となるポリマーは極限粘度が5以上、好ましくは10以上でありかつ、40未満であり、かつポリマーを常温固体でかつ融点が 100°C 未満の固形パラフィンに均一に溶解して10%溶液とした時の0.001sec $^{-1}$ および0.01sec $^{-1}$ のせん断速度で測定されたせん断粘度の比(すなわち前者を後者で割った値を以下本発明においては粘度指数と称する)が5以下、好ましくは3.5以下のポリマー(A)を90重量部以上99.9重量部未満、極限粘度が20以上、好ましくは25以上、さらにこのましくは30以上を有するより高分子量のポリエチレン(B)を0.1重量部以上10重量部未満含有してなる混合物を100重量部に対して、該ポリマー混合物を実質可溶な溶剤を100重量部以上添加して加熱して機械的混合を加えて溶解し、紡糸したのち延伸する手法により、最も効率的に上記目的に促した繊維を得ることができる。

【0014】本発明による新規な高強度ポリエチレン繊維は、前述のごとく温度による性能の変化が少ないことが特徴であり、この特徴は2種の力学分散すなわち、 α および γ 分散の温度で確実に定義することができる。通常 γ 分散は分子末端や側鎖などの局所的な分子鎖構造の欠陥に由来すると考えられてきた。通常、その分子鎖構造としてほとんど側鎖を有しない超高分子量ポリエチレンの場合、この寄与は主に分子鎖末端により影響されると考えられる。分子鎖末端が結晶構造の中あるいは周辺においてどのような分布を有するのかが学術的にも良く判明していない。当該発明者の検討によると、2種の超高分子量ポリエチレンを用いることが上記目的の達成のために推奨される。即ち、まずその極限粘度が5以上、好ましくは10以上でありかつ、40未満であり、そのポリマーを想定される溶解条件に準じて固形パラフィンに溶解して10%溶液とした時の粘度指数が5以下、好ましくは3.5以下のポリマー(A)を少なくとも90重量部以上99.9重量部未満含有し、これと極限粘度が20以上、好ましくは25以上、さらに好ましくは30以上を有する、より高分子量のポリエチレン(B)を0.1重量部以上、10重量部未満含有してなる混合物を100重量部に対して、該ポリマー混合物を実質可溶な溶剤を100重量部以上添加して加熱して機械的混合を加えて溶解し、紡糸したのち延伸する事により、上記 γ 分散温度を低温に維持したままで、 α 分散温度を高く

できることを見出し本発明に到達した。

【0015】その理由は推定でしかないが、粘度指数が5以下、好ましくは3.5以下であることは、せん断変形下での粘度のせん断速度の依存性が極めて小さいことを示唆する。このことは逆に言えば、緩和時間の非常に均一な分子が溶液流れ中に存在する（緩和時間分布が狭い）ことを示唆し結局、糸に成形される際に分子鎖がより均一に配列し分子末端構造が結晶中あるいはその近傍に均一に整列するのが原因ではないかと考えられる。通常のポリエチレンにおいては結晶化度が大きくなるほど、あるいは延伸倍率が大きくなるほど γ 分散温度は高くなるのが一般的に知られている。これは分子鎖末端等が結晶内部に取り込まれ、その運動が抑制されることを示唆すると考えれば、本繊維の γ 分散温度が比較的低温に維持されることは上記の機構を考えるに示唆的である。すなわち、何らかの分子の特異な整列機構によりポリエチレンの局所欠陥、主に分子鎖末端は結晶化や延伸とともに結晶内部に取り込まれること無く、むしろその周辺に偏在するのではないかと考えられる。このことは、結晶分散を表わす α 分散の温度が非常に高温になることもそれを指示するものであり、結晶内部に分子末端のような欠陥部が非常に少なく、結晶構造がより完全なものに近づいたことを示唆する。

【0016】本発明により粘度指数が5以下好ましくは3.5以下の超高分子量のポリマーを準備することは複数の手段により達成することができる。先ず第一は分子量分布の非常に少ないポリマーを用いることであり、例えば分子量分布 M_w/M_n が5以下のポリマーのなかから最適なポリマーを選択することができる。さらに好ましくは M_w/M_n は3以下であり、この場合は、例えばメタロセン触媒を用いて一段と分子量分布の狭いポリマーを用いても良い。さらに言えば分子量分布の M_w/M_n が5を超えるような、いわゆる通常のチグラー・ナッタ系触媒を用いたポリマーであっても、該ポリマーの溶解時において、そのポリマーのもともとの極限粘度 $[\eta_A]$ 、および繊維状態になった後の極限粘度 $[\eta_F]$ が次の式を満足するときほぼ本発明の要請する流動指数を満足することができる。

【0017】

$$[\eta_A] \times 0.60 \leq [\eta_F] \leq [\eta_A] \times 0.85$$

【0018】即ち、通常のチグラー・ナッタ系触媒によりほぼ限度まで分子量分布を狭く調整した超高分子量のポリエチレンをさらに溶解・押出しの工程で分子量を故意に低下させることにより、実質分子量分布を非常に狭くすることができる。この際、溶解工程で酸化防止剤を用いないことは当然ながら、過酸化化合物などの分解促進剤を添加したり、活性酸素を溶液に溶解するなどの処方は効率的である。このように、工程において分子を故意に劣化させると高分子量側がより切断される確率が高く、統計的に分子量分布が狭くなることが期待できる。

一方、本発明での要請はその流動指数にあり、流動改質剤や極少量のポリマーを添加して所望の流動指数を得てもよく、イオン性の凝集剤やステアリン酸金属塩などの流動改質剤は、それらの一例である。

【0019】さらに、本発明では上記主ポリマー(A)に対して少量部の極限粘度が20以上、好ましくは25以上、さらにこのましくは30以上を有する、より高分子量のポリエチレンを添加する処方を推奨する。この主旨は上記主ポリマーAだけでは温度に対する変化が少ない繊維を得ることができても、高強度繊維を得ることが困難であり、特に紡糸や延伸の過程において著しく分子の延伸性が悪くなる。鋭意検討の結果、極限粘度が20以上、好ましくは25以上、さらに好ましくは30以上を有する、より高分子量のポリエチレンを0.1重量部以上、10重量部未満のごく少量添加すると、著しく紡糸や延伸での変形が良好になるばかりか、より α 分散の温度も高くなり、力学特性、特に弾性率が大きく向上することが判明し本発明に到達した。

【0020】その原因は定かではないが、ごく少量の高分子量成分Bが紡糸や延伸の過程において必要最低限の応力伝播の役割を果たし、紡糸や延伸での分子の変形をスムーズにしたからではないかと推定しているが定かではない。Bの成分は極少量で良く10重量部を超えると逆に延伸等が極めて実施しにくくなるばかりか、溶解等での不均一の原因となる。一方、0.1重量部未満では、その成形性を向上させたり、熱的に安定化させる効果が十分でなくなる。

【0021】上記製法等により得られた繊維は、繊維状態での極限粘度 $[\eta_F]$ が5以上、好ましくは10以上、40未満であり、その強度が25 g/d以上、好ましくは30 g/d以上、更に好ましくは35 g/d以上、また弾性率が800 g/d以上、好ましくは1000 g/d以上、更に好ましくは1200 g/d以上であり、上述の力学分散特性との相乗効果により、実用面で従来にない極めて優れた特性を有するポリエチレン繊維を提供することを可能とした。

【0022】

【実施例】以下に本発明における特性値に関する測定法および測定条件を説明する。

（動的粘弾性測定）本発明における動的粘度測定は、オリエンテック社製「レオバイブロンDDV-01FP型」を用いて行った。繊維は全体として100デニール \pm 10デニールとなるように分繊あるいは合糸し、各単繊維ができる限り均一に配列するように配慮して、測定長（鉄金具間距離）が20 mmとなるように繊維の両末端をアルミ箔で包みセルロース系接着剤で接着する。その際の糊代ろ長さは、鉄金具との固定を考慮して5 mm程度とする。各試験片は、20 mmの初期幅に設定された鉄金具（チャック）に糸が弛んだり振じれたりしないように慎重に設置され、予め60℃の温度、110 Hzの

周波数にて数秒、予備変形を与えてから本実験を実施した。本実験では -150°C から 150°C の温度範囲で約 $1^{\circ}\text{C}/\text{分}$ の昇温速度において 110Hz の周波数での温度分散を低温側より求めた。測定においては静的な荷重を 5gf に設定し、繊維が弛まない様に試料長を自動調整させた。動的な変形の振幅は $15\mu\text{m}$ に設定した。

【0023】(強度・弾性率)本発明における強度、弾性率は、オリエンティック社製「テンシロン」を用い、試料長 200mm 、伸長速度 $100\%/ \text{分}$ の条件で歪一応力曲線を雰囲気温度 20°C 、相対湿度 65% 条件下で測定し、曲線の破断点での応力を強度(g/d)、曲線の原点付近の最大勾配を与える接線より弾性率(g/d)を計算して求めた。なお、各値は10回の測定値の平均値を使用した。

【0024】(極限粘度) 135°C のデカリンにてウベローデ型毛細粘度管により、種々の希薄溶液の比粘度を測定し、その粘度の濃度にたいするプロットの最小2乗近似で得られる直線の原点への外挿点より極限粘度を決定した。測定に際し、原料ポリマーのがパウダー状の場合はその形状のまま、パウダーが塊状であったり糸状サンプルの場合は約 5mm 長の長さにサンプルを分割または切断し、ポリマーに対して $1\text{wt}\%$ の酸化防止剤(商標名「ヨシノックスBHT」吉富製薬製)を添加し、 135°C で4時間攪はん溶解して測定溶液を調整した。

【0025】(せん弾粘度測定および粘度指数の計算)本特許におけるせん弾粘度測定方法について以下に詳しくその方法を記述する。まず超高分子量固形ポリマーを10重量部、および数平均分子量約 500 程度(融点が常温より高くその数平均分子量が 1000 を超えなければ良い)の固形パラフィン(本特許では粉末状固形パラフィン:商標名「LUVAX1266」:日本製蠟

(株)製を使用した)を90重量部および、ポリマーに対して実際に紡糸される条件の必要により $1\text{wt}\%$ の酸化防止剤(商標名「ヨシノックスBHT」吉富製薬製)を添加したものを、実際の紡糸における溶解条件にできるだけ準じて例えば2軸型混練り機等の装置を用いて、高温で混合・溶解し、押し出したものをペレット状にカットした。このようにして得られたペレットを 2mm のスペーサーを有する2対の平面金型内に充填し、予め 160°C に設定した加熱型プレス機にて1時間放置後、さらに $200\text{kgf}/\text{cm}^2$ の圧力を加えた状態で1時間放置した後、氷水にて急冷しテスト片を作成した。このテスト片をコーンプレート型の粘弾性測定装置(レオメトリックス社ARE S)に充填可能なサイズに切断し、 160°C で動的モードにてせん断速度 0.001sec^{-1} および 0.01sec^{-1} での複素動的粘度をそれぞれ求め、前者を後者で割った値をその粘度指数として採用した。測定はそのプレスした試験辺より10個所がランダムに選ばれ測定した結果の平均値である。

【0026】以下、実施例をもって本発明を説明する。

(実施例1)極限粘度が 18.5 でかつその分子量分布 $M_w/M_n=5.5$ の超高分子量ポリマーの主成分ポリマー(C)を98重量部と極限粘度が 30 でかつその分子量分布が約 $M_w/M_n=12.0$ のポリマー(D)を2重量部加えたパウダー状の混合物が全量の 15 重量%となるようにデカヒドロナフタレン 85 重量%を常温で添加した。このポリマーを2軸型の混合押し出し機にて 200°C の温度条件および 100rpm で溶解・押し出しを実施した。尚この際、酸化防止剤は使用しなかった。この操作を行う予備的な実験において前述のポリマー(C)単体を 10 重量%および 90 重量%の固形パラフィンを2軸型混練り機で 200°C で混合し同様のスクリー条件(温度および酸化防止剤を添加しないことを準拠)にて押し出した後、冷却して造粒したペレットを前述の評価法により粘度指数を計算したところ、その値は 3.2 であった。

【0027】かかるポリマーを上記の条件にて溶解後、 0.8mm 直径を有するオリフィスが48ホール設置された口金を用いて各ホールの吐出量が $1.6\text{g}/\text{min}$ となるように押し出して後、直ちに約 90°C の不活性ガスにて溶剤を一部除去しつつ、 $90\text{m}/\text{min}$ の速度で引き取りを実施した。引き取られた糸は直ちに 120°C のオープンにて5倍延伸されて後、一旦巻き取り、さらに 149°C に調整されたオープンにて4.5倍に延伸されて高強度繊維を得た。得られた繊維の動的粘弾性特性を含む諸物性を表1に示す。

【0028】(実施例2)実施例1における主成分ポリマーとして極限粘度が 22 のポリマー(E)を用いた他は、同様の操作で延伸糸を得た、流動指数を評価した。実施例1に比べ、延伸が非常にスムーズであり、高強度繊維が得ることができた。ポリマーEの粘度指数も 2.9 と更に良好な値が得られた。

【0029】(実施例3)実施例1における主成分ポリマー(C)と超高分子量成分ポリマー(D)の比率を 99.5 重量部および 0.5 重量部に変更した他はほぼ同等の操作で延伸糸を得た。ポリマーの流動指数は 3.1 であり、実験誤差の範囲で実施例1と同等であった。表1に示すように、若干、延伸性不良による強度の低下が見られ、又 γ 分散温度も若干高めの値が得られたが相対的には満足のいく結果が得られた。

【0030】(実施例4)実施例1の主成分ポリマーとしてジルコニウムメタロセンからなるエチレン重合体で、その極限粘度が 18.5 、および $M_w/M_n=2.7$ のポリマー(F)を用いる他は実施例1と同様の操作で延伸糸を得る実験を実施した。ポリマー(F)の流動指数は 1.9 と極めて優れた特性を示し、かつ延伸糸の物性は表1に示すごとく極めて優れたものが得られた。その理由は良く分からないが実施例1に比べて場合、弾性率が特に高い値を示した。動的粘弾性特性においても極めて優れた結果となった。

【0031】（実施例5）実施例4において、ポリマーを溶解する際にブレンドポリマーの総量に対して1wt%のBHTを添加した他は同様の操作で延伸糸を得る実験を実施した。本添加剤を処方した溶解方法に準拠して実施した流動指数は2.1と若干増加したが優れたものであった。得られた繊維の特性は実施例4に比較して低下したものの、実施例4で見られた強度に対する弾性率が高くなる傾向が見られた。又、動的粘弾性特性も優れた結果が得られた。

【0032】（比較例1）実施例1の主成分ポリマー（C）を用いた以外、高分子量物は添加しなかった。ポリマーCポリマーそのものの流動指数は当然実施例1と同等良好であり、強度・弾性率等は優れた値が得られたものの、相対的に γ 分散温度が高く、又 α 分散温度が低く、本特許が目指す広範囲の温度での物性変化の少ない繊維を得ることができなかった。

【0033】（比較例2）実施例4において主成分ポリマー（F）を用いた以外、高分子量物は添加しなかった。ポリマーFそのものの流動指数は当然実施例4と同等で極めて良好ではあるが、延伸や紡糸の過程で著しい糸切れが発生し、満足のできる十分な長さ（仮に100*

*0m以上連続で巻き取れたことで判断する。）の延伸糸が得られなかった。極く短時間巻き取ることが可能であった繊維の物性を表1に示す。強度・弾性率等はそここの値が得られたものの、比較例1と同様に γ 分散温度が高く、又 α 分散温度が低く、本特許が目指す広範囲の温度での物性変化の少ない繊維を得ることができなかった。

【0034】（比較例3）実施例1において、ポリマーを溶解する際にブレンドポリマーの総量に対して1wt%のBHTを添加した他は同様の操作で延伸糸を得る実験を実施した。本添加剤を処方した溶解方法に準拠して実施した流動指数は5.2と高い値が得られた。この流動指数が示す通り、紡糸・延伸では非常に高い頻度で糸切れが発生し、十分な長さの連続的な繊維を得ることができないばかりか短時間での採取も不可能であった。2段延伸倍率を2.5倍に低減して、短時間で得られた繊維の物性を表1に示す。強度・弾性率および動的粘弾性特性共に、低いレベルの延伸糸しか得ることができなかった。

【0035】

【表1】

実験	【 η_A 】	【 η_F 】 (g/dl)	流動指数	強度 (g/d)	弾性率 (g/d)	γ 分散温度 (°C)	α 分散温度 (°C)
実施例1	18.5	15.3	3.2	46.1	1521	-115	110
実施例2	22.0	14.9	2.9	47.5	1711	-118	112
実施例3	18.5	15.1	3.1	38.7	1233	-111	105
実施例4	18.0	15.1	1.9	49.5	1811	-119	115
実施例5	18.0	16.8	2.1	39.1	1611	-111	109
比較例1	18.5	15.1	3.2	43.8	1475	-105	97
比較例2	18.5	14.7	1.7	35.7	1211	-101	95
比較例3	18.5	16.7	5.2	23.1	754	-119	79

【0036】

【発明の効果】温度変化に対する繊維特性の変化が極めて

少ない各種用途に好適な高強度ポリエチレン繊維を提供することを可能とした。

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(54) **HIGH-STRENGTH POLYETHYLENE FIBER AND PROCESS FOR PRODUCING THE SAME**

(57) A high-strength fiber having an intrinsic viscosity of 5 or higher, a strength of 20 g/d or higher, a modulus of 500 g/d or higher, and dynamic viscoelasticity in which the γ dispersion loss modulus peak temperature is 100 degrees or lower and the loss tangent is 0.03 or lower. This fiber, which changes little in material properties with changing temperature and has excellent ordinary-temperature mechanical properties, can be efficiently provided by stretching a fiber spun from a 5 to

80 % solvent solution of a mixture comprising 99 to 50 parts by weight of a high-molecular polyethylene polymer A having an intrinsic viscosity of 5 or higher and a weight-average molecular weight/number-average molecular weight ratio of 4 or lower and 1 to 50 parts by weight of an ultrahigh-molecular polymer B having an intrinsic viscosity at least 1.2 times that of the polymer A.

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Description

Technical field

5 [0001] The present invention relates to high-strength polyethylene fibres which can be used in a wide range of fields, as various ropes, fishing lines, netting and sheeting for engineering, construction and the like, cloth and nonwoven cloth for chemical filters and separators, sportswear and protective clothing such as bulletproof vests, or as reinforcing material for composites for sport, impact-resistant composites and helmets, and particularly as various industrial materials used at from extremely low temperatures to room temperature; where the performance of said fibres, particularly 10 the mechanical properties such as strength and elastic modulus, undergo little variation with temperature during use in environments subject to large changes in temperature; and the present invention relates to a method for producing said fibres sufficiently quickly industrially.

Background technology

15 [0002] In recent years, active attempts have been made to obtain high-strength, high-elastic modulus fibres from ultrahigh molecular weight polyethylene starting material, and extremely high strength/elastic modulus fibres have been reported. For example, Japanese Unexamined Patent Application S56-15408 discloses a technique known as the "gel spinning method", where gel-like fibres obtained by dissolving ultrahigh molecular weight polyethylene in solvent are drawn to a high draw ratio.

20 [0003] It is known that the high strength polyethylene fibres obtained by the "gel spinning method" are very high in strength and elastic modulus as organic fibres, and are also highly superior in terms of impact resistance, and these fibres are being evermore widely used in various fields. The abovementioned Japanese Unexamined Patent Application No. S56-15408 discloses that it is possible to provide a material having extremely high strength and elastic modulus, 25 in order to obtain such high strength fibres. However, it is known that high strength polyethylene fibres undergo major changes in performance with temperature. For example, measuring the tensile strength while varying the temperature from about -160°C reveals a gradual decrease as the temperature increases, and that decrease in performance is particularly marked at from -120°C to around -100°C. With regard to temperature-related performance, then, it is anticipated that the performance of conventional high-strength polyethylene fibres could be considerably improved if their 30 physical properties at extremely low temperatures could be maintained at room temperature.

[0004] Conventional attempts to control changes in the mechanical properties of high-strength polyethylene fibres due to changes in temperature include an attempt to improve the vibration absorption at temperatures not greater than -100°C (referred to as the extremely low temperature region) by using a suitable ultrahigh molecular weight polyethylene starting material of a specific molecular weight and keeping the molecular weight of the resulting fibres within a 35 suitable range, as disclosed in Japanese Unexamined Patent Application No. H7-166414, but, fundamentally, that technique increases the mechanical dispersion at extremely low temperature. Specifically, it attempts to increase the variation in elastic modulus, whereas the present invention aims to lessen the deterioration in mechanical properties.

[0005] Japanese Unexamined Patent Application Nos. H1-156508 and H1-162816 disclose attempts to reduce the creep in high-strength polyethylene fibres by means such as ultraviolet irradiation and peroxides, in the abovementioned gel spinning method. It is noted that, fundamentally, this does decrease the mechanical dispersion in γ dispersion 40 as described above, which is described in the present invention as desirable, but both inventions aim to improve the creep of high-strength polyethylene fibres, but do not decrease the variation in mechanical properties due to changes in temperature. Specifically, if the relaxation strength in the γ dispersion is smaller, the temperature at which the relaxation occurs is usually shifted higher, and so as it is desirable in the present invention to decrease the variation in 45 mechanical properties that occur on changes in temperature, that is, to shift the γ dispersion temperature to a lower temperature, the conventional methods are contrary to the aim of the present invention.

[0006] Specifically, it is suggested that having a small γ dispersion value for γ dispersion temperatures in the range no greater than -100°C, as relaxation strength, while keeping the temperature therefor at very low temperatures allows the good physical properties (especially strength) seen in the very low temperature region to be maintained 50 without relaxation even for long periods at temperatures around room temperature, and such fibres would be extremely useful industrially. Fibres having such novel properties could, as described below, be substituted for conventional high-strength polyethylene fibres with no loss of the fundamental merits which said conventional fibres should have; moreover, as they are high-strength fibres, it is anticipated that they could also be drawn at extremely high speed during production processes and particularly during drawing processes. That is to say, this also has industrial significance as a novel production method which can yield high-strength polyethylene fibres of excellent performance at higher productivity. 55

[0007] In view of the situation described above, the present invention aims to provide high-strength polyethylene fibres characterized in that they have excellent mechanical properties at normal temperatures, and in that the mechan-

ical properties such as strength and elasticity modulus seen on wide temperature variation, particularly in the liquid nitrogen temperature region, are maintained at a high level even at room temperature; and a novel production method therefor.

5 Disclosure of the invention

[0008] The first invention of the present invention provides high-strength polyethylene fibres characterized in that they are polyethylene fibres comprising mainly ethylene component having an intrinsic viscosity $[\eta]$, when fibrous, of no less than 5, and have a strength of no less than 20 g/d and an elasticity modulus of no less than 500 g/d, and, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -110°C and the loss tangent ($\tan \delta$) is no greater than 0.03.

[0009] The second invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -115°C .

[0010] The third invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss tangent ($\tan \delta$) is no greater than 0.02.

[0011] The fourth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 100°C .

[0012] The fifth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 105°C .

[0013] The sixth invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that they have a strength of no less than 25 g/d and an elasticity modulus of no less than 800 g/d.

[0014] The seventh invention of the present invention provides high-strength polyethylene fibres according to Claim 1, characterized in that they have a strength of no less than 35 g/d and an elasticity modulus of no less than 1200 g/d.

[0015] The eighth invention of the present invention provides a method for producing high-strength polyethylene fibres, characterized in that a polymerization mixture comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component and having a weight average molecular weight to number average molecular weight ratio (M_w/M_n) of no greater than 4 and an intrinsic viscosity $[\eta]$ of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A), is dissolved in solvent to a concentration of from 5% by weight to 80% by weight, then spun and drawn.

[0016] The ninth invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the high molecular weight polymer (A) is a polyethylene polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (M_w/M_n) of no greater than 2.5 and an intrinsic viscosity $[\eta]$ of from 10 to 40.

[0017] The tenth invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the average intrinsic viscosity $[\eta]_M$ of the polymerization mixture is no less than 10 and the intrinsic viscosity $[\eta]_F$ of the resulting fibres satisfies the formula below

$$0.6 \times [\eta]_M \leq [\eta]_F \leq 0.9 \times [\eta]_M$$

[0018] The eleventh invention of the present invention provides a method for producing high-strength polyethylene fibres according to Claim 8, characterized in that the intrinsic viscosity $[\eta]_F$ of the resulting fibres satisfies the formula below

$$0.7 \times [\eta]_M \leq [\eta]_F \leq 0.9 \times [\eta]_M$$

[0019] The working mode of the present invention is described below.

[0020] The high molecular weight polyethylene of the present invention is characterized in that its repeat unit is essentially ethylene, although it may be a copolymer thereof with small amounts of other monomers such as α -olefin, acrylic acid or derivatives thereof, methacrylic acid or derivatives thereof or vinyl silane or derivatives thereof, or it may be a copolymer with these, or a copolymer with ethylene homopolymer, or it may be a blend with homopolymers of other α -olefins and the like. The use of a copolymer with an α -olefin such as propylene or butene-1 is particularly

preferred in that a degree of short or long chain branching imparts stability during the production of these fibres, particularly during spinning and drawing. However, too high a content of components other than ethylene has an adverse effect on drawing, and so in order to obtain fibres of high strength and high elasticity modulus, the monomer unit content should be no greater than 5 mol%, and is preferably no greater than 1 mol%. Obviously, homopolymer comprising

[0021] The characterizing feature of the present invention is, in essence, the provision of fibres characterized in that, in the temperature variance of the dynamic viscoelasticity properties measured when fibrous, the γ dispersion loss modulus peak temperature is no greater than -110°C , preferably no greater than -115°C , and the value of the loss tangent thereof ($\tan \delta$) is no greater than 0.03, preferably no greater than 0.02, and that the crystalline α dispersion loss modulus peak temperature is not less than 100°C , preferably not less than 105°C . The present invention also provides a method for obtaining fibres having these properties, that is, a method for producing high-strength polyethylene capable of essentially high speed drawing, at far higher productivity than conventional methods for producing the same kind of fibres.

[0022] The decrease in the temperature-dependent variation in the properties of the inventive fibres, particularly the excellent mechanical properties (particularly strength) at room temperature, can be defined in terms of the fibres' dynamic viscoelastic crystalline α dispersion peak temperature and γ dispersion peak temperature. Specifically, a marked decrease in elasticity modulus is usually seen in the temperature region in which mechanical dispersion occurs. In the case of high-strength polyethylene fibres, γ dispersion is usually observed around -100°C . At and beyond the limits of this γ dispersion, the physical values of polyethylene decrease markedly as the temperature is increased towards room temperature. For example, polyethylene fibres which are very strong (4 GPa) in an extremely low temperature atmosphere obtained using liquid nitrogen or the like (approximately -160°C) are less strong (their strength decreases to approximately 3 GPa) when measured at room temperature. Such an effect is obviously undesirable in products which involve the use of said fibres in wide temperature ranges, and it is thought that if this phenomenon could be improved upon, it would be possible to drastically improve strength at room temperature.

[0023] Moreover, high-strength polyethylene fibres exhibit a crystalline α dispersion at around 85°C , and even in this temperature region there is considerable variation in elastic modulus and strength, which is undesirable for various products. Accordingly, in order to allow a certain margin, the temperature range for the use of these fibres is usually decided by setting a temperature range between the γ dispersion temperature and the crystalline α dispersion temperature.

[0024] The lowering of the γ dispersion temperature and the raising of the crystalline α dispersion temperature is therefore highly significant in that it widens the abovementioned temperature range for use.

[0025] The γ dispersion is the first point scrutinized when aiming to develop new fibres based on this ideal design, and it is known that this γ dispersion originates from local defects at side chains, terminals and the like in the molecules which make up the fibres. Decreasing the number of defects would decrease the γ dispersion relaxation strength (that is, the loss tangent ($\tan \delta$)), but this would usually result in a more perfect fibre-fine structure, and so the temperature at which γ dispersion occurs would automatically shift to a higher temperature. Moreover, the crystalline α dispersion peak temperature in the present fibres is very high (at least 100°C or more, preferably 105°C or more) compared to that of conventional high-strength polyethylene fibres obtained by the abovementioned means such as drawing (which is at most 95°C). Furthermore, even if the abovementioned fibres which have a high crystalline α dispersion are excluded, it is difficult to achieve a temperature lower than -110°C in γ dispersion for highly crystalline fibres which usually have a crystalline α dispersion temperature of at least 90°C . Some fibres, for example those having a crystalline α dispersion temperature of around 85°C , do exhibit γ dispersion temperatures at or lower than -110°C , but this is because their fibre structure has become more amorphous, and such fibres are clearly distinguishable from the novel fibres targeted by the present invention, which have a high crystallinity (a high crystalline α dispersion temperature) and a low γ dispersion temperature.

[0026] Contrary to conventional technology, it is absolutely impossible to decrease the relaxation strength while the γ dispersion peak temperature is kept low. Given conventional common-sense, it is extremely surprising that the γ dispersion peak temperature in the fibres provided by the present invention is kept very low and that the value thereof is extremely small.

[0027] The means for obtaining the fibres of the present invention is necessarily a novel and cautious method. Moreover, the means described below provides high-strength polyethylene fibres of the present invention which also have the general characteristics of conventional high-strength polyethylene and so said means is also valuable industrially as a novel production method for these which achieves very high productivity.

[0028] The fibres of the present invention are obtained efficiently in practice by the abovementioned "gel spinning method", although provided that ultrahigh molecular weight polyethylene is moulded to yield known high-strength polyethylene fibres, any standard spinning technique may be used. The starting material polymer is of first importance in the present invention.

[0029] Specifically, the present invention recommends the use of a polymerization mixture of at least two types of

ultrahigh molecular weight polyethylene, comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (M_w/M_n) of no greater than 4 and an intrinsic viscosity $[\eta]$ of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A). Above all, polymer (A) should have an intrinsic viscosity of no less than 5, preferably no less than 10, but not more than 40, and the M_w/M_n of the polymer, measured by GPC (gel permeation chromatography), should be no greater than 4, preferably no greater than 3, and more preferably no greater than 2.5.

[0030] First, in order to achieve the inventive low value for the γ dispersion temperature, it is necessary to select a substance with as few defects as possible on the branches, terminals and the like, and so the degree of polymerization of the main polymer (A) is important, and if the intrinsic viscosity is less than 5, the molecular terminals increase considerably and the γ dispersion $\tan \delta$ value increases. If it exceeds 40, however, the viscosity of the solution becomes too great during spinning and spinning becomes difficult. Here, the average molecular weight (which represents intrinsic viscosity) and the distribution thereof, that is, the molecular weight distribution, are very important, and the M_w/M_n (measured by GPC) is preferably no greater than 4. By using a starting material which has an ultrahigh molecular weight and has a relatively uniform molecular weight distribution, it is easy to maintain a low γ dispersion temperature and have a low $\tan \delta$ value thereof.

[0031] The reason for this is not well understood, although it is speculated that when the molecular chain is made uniform, crystals (thought to be formed by the extending of the chains) cause the molecules to line up and become oriented, and so there are very few molecular terminals in the crystalline region, and the molecular terminals collect and remain in the so-called amorphous region. That is, it is speculated that the crystalline region, which makes up most of the inventive fibre structure, becomes more perfectly crystalline, with fewer defects, and the components such as molecular terminals concentrate in the amorphous region. This corresponds with the scientifically known fact that if the crystalline region contains many defects (which dictate the γ dispersion), the peak temperature will shift to a higher temperature, and with the fact that there are few local regions of molecular terminals and the like in the crystalline part of fibres of the present invention. As the main structure of the inventive fibres is a crystalline structure comprising extended chains, it is thought that the molecular terminals concentrate in the amorphous part and do not particularly affect physical properties, although this is a hypothesis contrived to explain the effects of the present invention and is not certain.

[0032] Thus by merely using an ultrahigh molecular weight polyethylene polymer having an extremely narrow molecular weight distribution in a common spinning method, stable discharge cannot be achieved during spinning because the molecular weight distribution of the starting material polymer is very narrow, and the discharged solution has almost no extendability and so moulding it is impossible in practice. The molecular weight distribution M_w/M_n should at least be greater than 4 when an abovementioned polymer is supplied to a conventional gel spinning method. An example of an attempt to use such a low molecular weight polymer is disclosed in Japanese Unexamined Patent Application No. H9-291415, wherein high strength, high elasticity modulus fibres are obtained using an ultrahigh molecular weight polyethylene-based polymer that is prepared using a special catalyst and has a viscosity average molecular weight of no less than 300,000 and an M_w/M_n ratio of no greater than 3. According to said publication, the technique disclosed therein is commonly employed, rather than the gel spinning method which is commonly used to produce high-strength polyethylene fibres; said disclosed technique involves a combination of solid phase extrusion and gel extension using a dry simple crystal aggregate reagent, where said simple crystal aggregate is obtained by dissolving polymer to a dilute solution of a concentration of no more than 0.2 wt%, and technology involving the use of a simple crystal aggregate is also disclosed in the working example. As shown in this example, it is extremely difficult to perform spinning and drawing processes using the low M_w/M_n polymer of the conventional gel spinning method. Needless to say, the general properties and physical properties of the gel drawn films made from the very dilute solutions disclosed in said publication are different from those of the novel fibres provided by the present invention.

[0033] The reason why it is difficult to mould such polymers having a very narrow molecular weight distribution is perhaps that the intertwining of molecular chains is drastically reduced as a result of the narrow molecular weight distribution, and so the stress required to deform the molecular chains during spinning and drawing cannot be uniformly transmitted, although this is merely speculation. With this in mind, diligent research was performed into improving conventional technology, and the present invention was achieved on discovering that the use of a mixture comprising from 99 to 50 parts by weight of polymer (A) (main component) and from 1 to 50 parts by weight of ultrahigh molecular weight polymer (B) having an intrinsic viscosity that is at least 1.2 times that of polymer (A) greatly facilitates spinnability (facilitates take-up when the solution discharged from the spinneret is drawn) and drawing, and markedly improves drawing speed, and the resulting fibres have the required properties described above, that is, the γ dispersion temperature is low and $\tan \delta$ is low. Furthermore, in the present invention, by using a mixture in which the average intrinsic viscosity $[\eta]M$ of the polymers therein is not less than 10, and by dissolving the polymer in solvent so that it comprises from 5% by weight to 80% by weight of the total, and spinning and drawing under production conditions so that the

intrinsic viscosity $[\eta]F$ of the resulting fibres satisfies the equation below, it is possible to obtain fibres having physical properties that are remarkably close to those desired:

$$0.6 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

preferably,

$$0.7 \times [\eta]M \leq [\eta]F \leq 0.9 \times [\eta]M$$

[0034] It is not certain how this relationship between the molecular weight of the starting material polymers and the resulting fibres affects the physical properties of the fibres, but if the intrinsic viscosity $[\eta]F$ of the fibres exceeds 90% of $[\eta]M$, the two different molecular weight polymers do not uniformly mix and extendability is extremely poor, whereas if $[\eta]F$ is less than 70% of $[\eta]M$, mixing two polymers has almost no effect and it is only possible to achieve more or less the same physical properties as seen in high strength polyethylene fibres in which the molecular weight distribution is as wide as usual. A large difference between the degree of polymerization of the resulting fibres and the starting material polymer means that the molecular chains break during processing, and the molecular weight distribution has to be somehow readjusted. It has been suggested that at this time the polymer of high molecular weight within the mixture often deteriorates more, and that by adjusting the molecular weight distribution of the whole so that this high molecular weight matter is incorporated in the low molecular weight matter molecular weight distribution region, a smoother molecular sequence is obtained, and, as the residual high molecular weight component fulfils its role of spreading tension during moulding, both mouldability and workability during spinning and drawing are achieved, although this is speculation and has not been confirmed.

[0035] Fibres obtained by the abovementioned methods have an intrinsic viscosity $[\eta]F$, when fibrous, of no less than 5, preferably from 10 to 40, a strength of no less than 20 g/d, preferably no less than 25 g/d, and more preferably no less than 35 g/d, and an elastic modulus of no less than 500 g/d, preferably no less than 800 g/d, more preferably no less than 1200 g/d, and, as a result of synergistic effects with mechanical dispersion properties as described above, it is possible to provide polyethylene fibres of excellent properties for practical use, which are not known conventionally.

Optimum mode of the present invention

[0036] The present invention is described below by means of working examples, but the present invention is not limited to these.

[0037] The measurement methods and measurement conditions for the property values in the present invention are described first.

Dynamic viscoelasticity measurement

[0038] In the present invention, dynamic viscosity was measured using a Rheovibron DDV-01FP, manufactured by Orientec. The fibres as a whole were divided or doubled to have 100 denier \pm 10 denier, and while the respective fibres were arranged as uniformly as possible, both the terminals of the fibres were enclosed with aluminium foils such that the measurement length (distance between the chuck ends) was 20 mm, and the fibres were adhesive-bonded with a cellulose type adhesive. The length of the margin left for applying the adhesive was made around 5 mm to allow fixing of the chuck. Each test sample was set carefully on the chuck at an initial width of 20 mm to prevent the strand from being entwined or twisted around it, then the fibres were subjected to preliminary deformation for a few seconds at a temperature of 60°C and a frequency of 110 Hz. In this experiment, the temperature distribution was determined at a frequency of 110 Hz in the range of from -150°C to 150°C, increasing the temperature from -150°C at a rate of approximately 1°C/min. During measurement, the stationary load was set at 5 gf and the sample length was automatically controlled to prevent the fibres from loosening. The dynamic deformation amplitude was set at 15 μ m.

Strength/elastic modulus

[0039] In the present invention, the strength and elastic modulus of a 200 mm-long sample were determined using Tensilon, manufactured by Orientec, at a draw rate of 100%/min, and the distortion-stress curve was obtained at an atmospheric temperature of 20°C and 65% relative humidity; the stress (g/d) at the break point in the curve was determined, and the elastic modulus (g/d) was calculated from the tangent of the line giving the maximum slope in the vicinity of the origin of the curve. Each value was the average of 10 measurements.

Intrinsic viscosity

[0040] The relative viscosities of various dilute solutions in decalin at 135°C were measured using an Ubbelohde type capillary viscosity tube, and the intrinsic viscosity was determined from the extrapolation point towards the origin of the straight line obtained by least square approximation of plots of viscosities against concentration. For these measurements, if the starting material polymer was powdery it was used in that form without further modification, whereas in the case of lumpy powder or fibrous samples, solutions for measurement were prepared by dividing or cutting the samples to approximately 5 mm in length, adding antioxidant (Yoshinox BHT, manufactured by Yoshitomi Seiyaku) at 1 wt% with respect to the polymer, then dissolving with agitation for 4 hours at 135°C.

Molecular weight distribution measurement

[0041] For this patent, Mw/Mn was measured by the gel permeation chromatography method. Measurements were made at a temperature of 145°C using a 150C ALC/GPC instrument manufactured by Waters, and GMHXL series column manufactured by Tosoh (K.K.). The calibration curve for the molecular weight was obtained using a polystyrene high molecular weight calibration kit manufactured by Polymer Laboratories. The sample solutions used were obtained by dissolving in trichlorobenzene to 0.02 wt%, adding antioxidant (Irgafos 168, manufactured by Ciba Geigy) at 0.2 wt% of the polymer, then dissolving for approximately 8 hours at 140°C.

[0042] The present invention is described in detail below.

Working Example 1

[0043] A powder mixture comprising 99 parts of homopolymer (A) of ultrahigh molecular weight polyethylene having an intrinsic viscosity of 18.5 and a molecular weight distribution index Mw/Mn of 2.5 and 2 parts by weight of polymer (D) having an intrinsic viscosity of 28.0 and a molecular weight distribution Mw/Mn of approximately 5.5 was taken, and 70% by weight of decahydronaphthalene was added at normal temperature so that said mixture made up 30% by weight of the total. At this time, the intrinsic viscosity $[\eta]M$ of the polymer mixture was 18.8. A decalin dispersion of this mixed polymer was supplied to a twin-screw mixer/extruder and dissolved and extruded at 200°C and 100 rpm. It should be noted that antioxidant was not used at that time.

[0044] Solution prepared in this way was extruded using a spinneret provided with 48 holes of orifice 0.6 mm in diameter such that the output from each hole was 1.2 g/min, then part of the solvent was immediately removed using inert gas adjusted to room temperature, and the sample was taken off at a rate of 90 m/min. Immediately after having been taken off, the polymer content of the gel-like fibres was 55% by weight. This yarn that had been taken off was immediately drawn 4-fold in a 120°C oven, then wound once, then further drawn 4.5-fold in an oven adjusted to 149°C, to yield high-strength fibres. The various physical properties, including the dynamic viscoelasticity, of the resulting fibres are shown in Table 1.

Working Example 2

[0045] Spun yarn was obtained by the same operations as in Working Example 1, except that polymer having an intrinsic viscosity of 12.0 was used as the main component polymer. At this time, the intrinsic viscosity $[\eta]M$ of the polymer mixture was 10.6. Drawing was much smoother than in Working Example 1, but the strength of the resulting fibres was slightly lower.

Working Example 3

[0046] The proportion of the main component polymer of Working Example 1 and the added polymer was adjusted to 90 parts by weight: 10 parts by weight, then spun yarn was obtained by the same operations. At this time, the intrinsic viscosity $[\eta]M$ of the polymer mixture was 19.5. The second drawing was slightly awkward and the draw ratio had to be dropped to 4-fold, and as a result the strength and elasticity modulus and the like were lower, although it was possible to obtain fibres having physical properties which were satisfactory overall.

Working Example 4

[0047] An experiment was performed which involved obtaining spun yarn by the same operations as in Working Example 1, except that when the polymer was dissolved, antioxidant (trade name Yoshinox BHT, manufactured by Yoshitomi) was added at 1 wt% with respect to the total amount of blend polymer. The spinning speed was increased to an upper limit of 30 m/min, and thereafter relatively stable drawing was possible. The properties of the resulting

fibres were compared with those achieved in Working Example 1, and although the elasticity in particular was lower, overall satisfactory results were obtained.

Working Example 5

[0048] Fibres were obtained by the same operations as in Working Example 1, except that polymer having an intrinsic viscosity of 18.2 obtained by copolymerizing 1-octene at 0.1 mol% with respect to ethylene was used as the main component polymer. It should be noted that the intrinsic viscosity of the mixture was 18.5. the elasticity of the fibres tended to be slightly lower than those obtained in Working Example 1, although when it came to spinning, the spinnability and the workability on extension and the like were superior. The dynamic viscoelasticity was also excellent.

Comparative Example 1

[0049] Only the main component polymer of Working Example 1 was used, and no high molecular weight material was added. Spinning resulted in immediate serious yarn breakage and it was impossible to pick up satisfactory fibres.

Comparative Example 2

[0050] 0.2% by weight of main component polymer (A) used in Working Example 1 were taken, antioxidant (trade name Yoshinox BHT, manufactured by Yoshitomi) was added to 1 wt% with respect to the polymer, and these were dissolved uniformly in decalin, then casting was performed on a flat surface glass plate which was then left naturally overnight, then the solvent was completely evaporated off by leaving the system in a vacuum at 80°C over 2 nights, to yield an approximately 15 micron thick cast film. This was drawn 4-fold at 50°C, 3-fold at 120°C and then 2-fold at 140°C to a total of 240-fold at a distortion speed of approximately 10 mm/min using a tension tester with provision for high temperatures, to yield a highly oriented film. The strength of the resulting film, calculated as (g/d) is shown in Table 1. The dynamic viscoelasticity of the film was measured by measuring according to the measurement method for fibres corresponding to the dimensions and thickness of the sample, then performing final correction to the actual thickness. The properties of the resulting film were such that it had sufficient high strength and high elasticity modulus. Specifically, the elasticity modulus was particularly excellent, as seen from the high draw rate. As for its dynamic viscoelasticity, although the γ dispersion value was low, its peak temperature shifted to an extremely high temperature and it was impossible to achieve the desired physical properties.

Comparative Example 3

[0051] Drawn yarn was obtained by the same operations except that polymer having an intrinsic viscosity of 18.8 and a molecular weight distribution index M_w/M_n of 8.5 was used instead of the main component polymer used in Working Example 1. It should be noted that the average intrinsic viscosity of the blend was 18.9. the yarn extendability was less than that achieved in Working Example 1 and it was necessary to decrease the draw ratio slightly, and so the strength was lower. As for the dynamic viscoelasticity, the γ dispersion loss modulus peak value temperature was good, at -116°C, although the loss tangent was a high value, at 0.040.

Industrial uses

[0052] It is possible to provide high-strength polyethylene fibres which can be used in a wide range of fields, as various ropes, fishing lines, netting and sheeting for engineering, construction and the like, cloth and nonwoven cloth for chemical filters and separators, sportswear and protective clothing such as bulletproof vests, or as reinforcing material for composites for sport, impact-resistant composites and helmets, and particularly as various industrial materials used at from extremely low temperatures to room temperature; where the properties of the fibres change very little with temperature variation and where said high-strength polyethylene fibres have excellent mechanical properties at normal temperature. It is also possible to provide a method for producing these high-strength polyethylene fibres with sufficiently quickly speed industrially.

Table 1

Experiment	$[\eta]B$ (g/dl)	$[\eta]F$ (g/dl)	Draw rate	Strength (g/d)	Elasticity modulus (g/d)	γ dispersion temperature (°C)	$\tan \delta$ (-)	Crystalline α dispersion temperature (°C)
Working Example 1	18.8	15.2	18	43.1	1557	-114	0.021	110
Working Example 2	12.7	10.3	18	32.5	1025	-119	0.028	105
Working Example 3	19.6	16.3	16	45.2	1533	-112	0.025	112
Working Example 4	18.8	17.2	18	34.6	918	-111	0.029	107
Working Example 5	18.2	18.5	18	41.1	1235	-116	0.024	108
Comparative Example 1	18.5	-	-	-	-	-	-	-
Comparative Example 2	18.5	17.8	240	44.7	1905	-98	0.022	95
Comparative Example 3	18.9	15.5	17.5	33.5	1103	-116	0.040	83

Claims

1. High-strength polyethylene fibres **characterized in that** they are polyethylene fibres comprising mainly ethylene component having an intrinsic viscosity $[\eta]$, when fibrous, of no less than 5, and have a strength of no less than 20 g/d and an elasticity modulus of no less than 500 g/d, and, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -110°C and the loss tangent ($\tan \delta$) is no greater than 0.03.
2. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss modulus peak temperature is no greater than -115°C .
3. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the γ dispersion loss tangent ($\tan \delta$) is no greater than 0.02.
4. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 100°C .
5. High-strength polyethylene fibres according to Claim 1, **characterized in that**, in the measurement of the temperature variance of the dynamic viscoelasticity of the fibres, the crystalline α dispersion loss modulus peak temperature is no less than 105°C .
6. High-strength polyethylene fibres according to Claim 1, **characterized in that** they have a strength of no less than 25 g/d and an elasticity modulus of no less than 800 g/d.
7. High-strength polyethylene fibres according to Claim 1, **characterized in that** they have a strength of no less than 35 g/d and an elasticity modulus of no less than 1200 g/d.
8. Method for producing high-strength polyethylene fibres, **characterized in that** a polymerization mixture comprising from 99 to 50 parts by weight of (A) and from 1 to 50 parts by weight of (B), where (A) is high molecular weight polymer comprising mainly ethylene component and having a weight average molecular weight to number average molecular weight ratio (M_w/M_n) of no greater than 4 and an intrinsic viscosity $[\eta]$ of no less than 5, and (B) is an ultrahigh molecular weight polymer having an intrinsic viscosity at least 1.2 times that of high molecular weight polymer (A), is dissolved in solvent to a concentration of from 5% by weight to 80% by weight, then spun and drawn.
9. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the high molecular weight polymer (A) is a polyethylene polymer comprising mainly ethylene component having a weight average molecular weight to number average molecular weight ratio (M_w/M_n) of no greater than 2.5 and an intrinsic viscosity $[\eta]$ of from 10 to 40.
10. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the average intrinsic viscosity $[\eta]_M$ of the polymerization mixture is no less than 10 and the intrinsic viscosity $[\eta]_F$ of the resulting fibres satisfies the formula below

$$0.6 \times [\eta]_M \leq [\eta]_F \leq 0.9 \times [\eta]_M$$

11. Method for producing high-strength polyethylene fibres according to Claim 8, **characterized in that** the intrinsic viscosity $[\eta]_F$ of the resulting fibres satisfies the formula below

$$0.7 \times [\eta]_M \leq [\eta]_F \leq 0.9 \times [\eta]_M$$

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/02766

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ D01F6/46		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ D01F6/46		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1995 Jitsuyo Shinan Toroku Koho 1996-1999		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 1-156508, A (Toray Industries, Inc.), 20 June, 1989 (20. 06. 89) (Family: none)	1-7
A	JP, 1-162819, A (Toray Industries, Inc.), 27 June, 1989 (27. 06. 89) (Family: none)	8-11
A	JP, 7-166414, A (Toyobo Co., Ltd.), 27 June, 1995 (27. 06. 95) & US, 5443904, A	1-11
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 24 August, 1999 (24. 08. 99)		Date of mailing of the international search report 7 September, 1999 (07. 09. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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